DETECTION TECHNIQUES FOR TENUOUS PLANETARY ATMOSPHERES

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INTRODUCTION AND SUMMARY

This report will cover the work performed from January 1, 1966 to June 30, 1966 on Grant NsG-458 between The University of Arizona and the National Aeronautics and Space Administration.

This contract was set up to support the development of new types of detectors for analysis of planetary atmospheres. Initially the interest was in detectors for use under partial vacuum conditions; recently, the program has been extended to include detectors for use at one atmosphere.

Results to date have included detectors for O_2, H_2 and CO under partial vacuum conditions, (see references section). More recently, detectors for H_2 and CO in air at atmospheric pressure have been reported, but as yet no publications have appeared in the journals.

This semi-annual report will discuss our work on a new detector for ammonia vapor in air. We will also review the status of the hydrogen detector program and discuss the first results of our studies of semiconductor detectors for gases.

RESULTS

The Ammonia Vapor Detector

In earlier reports we mentioned that the reaction of ammonia vapor with alpha brass was quite specific and might serve as a detector for NH_3. The reaction itself has been under study on another program (supported by State Funds) because of our basic interest in stress corrosion. As part of this work we were able to show that the NH_3/Alpha brass reaction could be controlled by the application of electrostatic potentials.

The system, as modified for detection of ammonia, is shown in Fig. 1. For operation a controlled mixture of NH_3, water vapor and a

gas (air) is passed (at room temperature) through the detector. After five minutes of operation the ion current, from the alpha brass wire to the collector, is measured. This current is directly proportionate to the partial pressure of ammonia.

The first results are shown in Fig. 2 where the ion current, after five minutes, is shown versus the ratio of NH_3 to air by weight. The curve is quite linear above 1% and we feel that a definite improvement is possible for ratios of NH_3/air below 1%. A 1% mixture by weight represents a 1.6% mixture by volume. This is far above the maximum ammonia concentration permitted in room air (usually stated as 100 ppm or 0.01% by volume [10]). These experiments were run at a wire potential of +200V DC; we feel that the sensitivity can be substantially increased by higher voltages and pretreatment of the wire. This will be an objective in the next six-month period of the contract.

The system is completely insensitive to water vapor, argon, oxygen, nitrogen, hydrogen or helium. The repeatability is quite satisfactory and the system is not sensitive to the ambient temperature within reasonable (20^oC - 95^oC) limits.

The presence of water vapor does not seem to be a requirement; the detector works even with anhydrous ammonia, but water vapor does seem to shorten the induction period before the positive ion current begins to flow.

The exact nature of the ions is not yet clear, but we have a strong suspicion that they are Zn^+ or a zinc-ammonia complex. This arises from the fact that after several hours of operation a metallic zinc deposit appears \ on the collector.

The ammonia detector is a most useful device and we intend to extend the calibration and if possible improve the sensitivity. However, our major interest will be in the study of the physics of the reaction. The

processes of stress corrosion are still unclear and this will be the area of Mr. Herman Sulsona's Ph.D. thesis in Mechanical Engineering.

The ammonia detector may have potential for detection of protein molecules. The decomposition of protein produces ammonia and this phenomenon might be utilized for detection purposes. As a simple test of this idea, we made up a 1% water solution of urea. If several drops of this solution were placed on the brass wire, the usual ammonia reaction was observed when the urea was decomposed by heating ($\sim 90^{\circ}C$). A controlled experiment with pure water yielded no current under the same conditions.

Indications are that microgram quantities of protein can be detected by this technique. We have discussed this work with scientists at Jet Propulsion Laboratoryr who are concerned with life detection on the planets. Since protein material is a strong indication that living matter has existed, a simple technique for detection of protein may be of importance.

If there is any interest in this technique, we will cooperate in the further development of a protein detector. However, we recognize that this is only a secondary interest for the detectors program.

Semiconductor Detectors

Semiconductors have great potential for use as gas detectors and we have begun some research in this area. Our first efforts were devoted to developing reliable fabrication and testing techniques on a "simple" semiconductor, ZnO.

Zinc oxide has been studied in great detail[1] and its properties are considered well known. Its use as a detector has been reported by Seiyama[2] where response to H_2, O_2 and some hydrocarbons was discussed. ZnO is quite easy to make and is not as sensitive to processing techniques

as is silicon. Later, when we are more experienced in the use of semiconductors, we will be able to investigate materials like silicon for detection purposes.

To discuss our results in this area we must quickly review some pertinent semiconductor theory.

Semiconductors differ from metals in two ways; first, they have relatively few charge carriers. Second, the allowed electron energies do not form a continum but are in bands, separated by regions of forbidden energy in which no charge carriers can exist.

The lower allowed (valence) band is generally filled with electrons (at room temperature) while the upper allowed (conduction) band is essentially empty. The material may be "doped" with impurities which either donate an electron to the conduction band (n type) or acquire an electron from the valence band (p type), thereby leaving a hole.

This picture must be modified as the surface is approached[3]. The surface may have available energy states in the normally forbidden energy band. These surface states can trap electrons which would otherwise be free in the conduction band and the surface is then spoken of as being depleted since near the surface the conduction band lacks its normal quota of electrons. On the other hand, there may be extra free electrons available near the surface and the surface is then spoken of as an accumulation region.

The fact that surface states can be induced or modified by exposure of the semiconductor to various gaseous ambients, is the reason that semiconductors can be used as gas detectors. An important point here is the fact that semiconductors have relatively few charge carriers and only a small number of absorbed molecules are needed to make a significant change in the properties of the material. This is in contrast to metals where

absorbed ambient gases have very little effect, in general, on the bulk metal properties.

To return to zinc oxide, we note that the material can be fabricated into thin films having a zinc rich ZnO structure. This is done by evaporation of zinc onto glass slides* which are then oxidized in air at about 400°C until all the metallic zinc is converted into transparent zinc oxide.

The resultant material is an n type semiconductor which means that it has a significant number of electrons in the conduction band. Now if the ZnO is exposed to an ambient gas which absorbs on the surface and donates electrons, the conductivity of the material will increase. If, on the other hand, the absorbed gas is an electron acceptor, the conductivity will decrease.

In any case the fact that the ZnO is in thin film form means that surface effects will be significant and the ambient gas will be able to diffuse in and out of the ZnO rather quickly.

The fact that gases differ in the degree to which they are absorbed and in whether they are donors or acceptors allows certain semiconductors to be used as specific detectors.

The general problem, then, is to develop semiconductor detectors which are rapid in response, linear in output, repeatable when cycled and specific to a certain gas.

Results on Zinc Oxide

It should be noted here that we are to some extent repeating the work of Ref. 1 and 2. We must gain experience in this area and our interests are somewhat different than those of other workers. We hope to build detectors and therefore we must study the effect of ambient gases in much

more detail than that reported in Ref. 1 and 2.

At this point we are interested in the general properties of the material. Evaluation of ZnO as a specific detector will come later when we understand its properties in more detail.

In Fig. 3 we show the response of a thin film of ZnO to a sudden change in ambient gas pressure. In this case the film was held at 250°C and the gas was air. Two hundred fifty degree Centigrade or higher temperatures seem to be needed for thermal excitation of electrons from the valence to the conduction band. At room temperature the electrical conductivity of ZnO is much lower and there is little or no effect of ambient gases.[*]

Figure 3 shows a rapid drop in current (conductivity) with admission of dry air, followed by a slow further decrease to an equilibrium value. The effect is due almost entirely to oxygen. Oxygen is an acceptor when adsorbed and reduces the number of free carriers in the ZnO.

In Fig. 3 we also show a curve for dry N_2; there is no detectable change in the current, which agrees with the results of Ref. 2 and our suggestion that the change in current upon admission of air was due entirely to the effect of oxygen.

Figure 3 displays another typical phenomenon of semiconductor detectors, "fast" and "slow" states. To explain this we must digress for a moment to more semiconductor physics.

When an acceptor is adsorbed on an n type semiconductor, some of the electron traps produced lie below the conduction band and are quickly filled by conduction electrons. This causes the rapid drop in current shown in Fig. 3.

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[*] One would think that when the film is at room temperature, adsorption would be more effective in changing the conductivity, since there are fewer charge carriers. The observed effect may indicate a temperature effect in adsorption.

There also exist electron traps which are separated by an energy barrier from the conduction band electrons. As the electrons are thermally excited over the barrier they drop into the traps and this produces the slow decrease in current shown in Fig. 3.

The existence of fast and slow states limits the response time of semiconductor detectors and this may be a serious handicap to the use of such detectors for certain space applications. However, operation at higher temperatures $\sim 400^{\circ}C$ appears to speed up the thermalization of slow states to their final equilibrium value. An important part of our investigation will be a gaining of information about these poorly understood, slow states and of methods for speeding up their approach to equilibrium.

Earlier we noted that most of the conductivity change in ZnO, upon exposure to air, was due to oxygen. As further evidence of this, we show in Fig. 4 the conductivity of ZnO when cycled at one Atm. between dry air and dry nitrogen. The repeatability is very good and it may be possible to use ZnO as an oxygen monitor in air. Again the distinct difference between the effects of air and nitrogen are in agreement with the results of Ref. 2 which indicate that nitrogen has very little effect on the conductivity of ZnO. The higher temperature ($300^{\circ}C$) does reduce the time necessary to achieve equilibrium.

In Fig. 5 we show the change in current (conductivity) as a function of ambient pressure for dry air and nitrogen. Again we see that there is a change in conductivity upon exposure to air, which is proportionate to the ambient oxygen pressure.

The current vs. pressure curve for air is not of constant slope but we hope to improve this as we gain further experience with ZnO.

The current vs. pressure line for N_2 is quite straight and shows a slight increase in current with pressure. This, we think, is due to thermodynamic exchange of previously adsorbed oxygen from an earlier experiment with air.

From the results discussed above it seems quite reasonable to suggest that ZnO systems may be quite useful for gas detectors. More work will be needed, especially to speed up the "slow states" in their approach to equilibrium but we have confidence that this will be possible.

This completes the reports on the ZnO work to date. In a later section we will discuss plans for further studies on ZnO.

Surface Ionization Detector For Hydrogen in Air at One Atmosphere

In our last report we discussed the recent results with the hydrogen detector. The response of the device was shown to be quite linear and we have begun a detailed study of phenomena involved in the production of the ion current.

Earlier we suggested that the ion current was due to H_2^+ or H^+ ions produced on the palladium surface. However, a recent paper by Howling[4] has proposed that the alkali ion current is due essentially to K and N_a from the glass in the experimental system.

In contrast, two reports from the Soviet Union, Ref. 5 and 6, indicate that the current is due to alkali ions coming from the hot filament itself. This does, in fact, seem the most plausible source for the current. However, the mechanism is poorly understood. For example, Ref. 5 suggests that O_2 reduces the ion current while H_2 increases it. This agrees with our results; however, if the current is produced by surface ionization of alkalis, this indicates that O_2 must lower the surface work function while H_2 must

cause the work function to _increase_. This effect of O_2 and H_2 is exactly opposite to that normally observed[7] and this is one of the reasons we suggested a H^+ or H_2^+ ion mechanism in our last report.

The entire question of how the surface ionization current is generated will be the subject of a Ph.D. thesis in Mechanical Engineering by Mr. Jay Abramowitz. Construction of a mass spectrometer and an ion diffusion system has been started and experiments will begin in the Fall when Mr. Abramowitz returns.

The problem of determining the e/m ratio, for the ions emitted by hot palladium, is not an easy one. Our first attempts, with simple types of apparatus, failed because of the low ion currents available. For this reason the mass spectrometer is under construction.

We have had some correspondence with the NASA center in Huntsville, Alabama regarding the use of the hydrogen detector in the Saturn vehicle. The problem seems to be one of the design of an appropriate operational system and testing of the detector under the usual vibration, shock and environmental specifications for Space.

These requirements are obviously beyond our capabilities and we have been discussing these problems with several commercial firms. If it appears that one of these firms is interested in packaging the H_2 detector for the Saturn system we will cooperate with them as much as possible.

Operations with Other Space Related Activities

In earlier reports we have mentioned cooperative efforts with the University of Arizona Lunar and Planetary Laboratory. This work is continuing, a vacuum furnace for melting of such materials at $1300^\circ C$ is in operation[*]

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[*] See References 6 and 7.

and LPL personnel are using this facility to study size effects on rock frothing during melting.

Another group from the LPL is using a DC plasma discharge[*] to study sputtering and color changes in various rock samples. Both of these programs are directed toward a better understanding of the lunar surface and the geological history of the moon.

In both these programs the LPL pays for all apparatus and supplies used on their studies. Certain permanent apparatus, like the 18" x 22" vacuum system constructed on NsG-458, is furnished by the FESS Laboratory. We share a technician and to date this cooperative effort has proved most satisfactory. We expect to continue it in the future.

Future Plans

We hope to continue the work on ZnO, first to operate at higher temperatures and, second, to test the response to other gases.

ZnO is sensitive to water vapor but its recovery is quite slow when the ambient water vapor is removed. Operation at higher temperatures may alleviate this problem.

ZnO is sensitive to hydrogen and we hope to run tests in mixtures of hydrogen and air or nitrogen to see if a potential for hydrogen detection exists.

The Department of Electrical Engineering is finishing a facility for work on semiconductor circuits. This will give us access to facilities for handling silicon. There is great interest in silicon surface properties, primarily because of the semiconductor industry and secondarily because of its potential for gas detection. We have been in correspondence with Dr. T. M. Buck of the Bell Telephone Laboratories. He has been most helpful

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[*] See References 6 and 7, under Publications.

in supplying detailed information about his studies on effects of gases
on semiconductor properties, Ref. 8,9.

If all goes well, we will be able to begin studying silicon in
the Fall of 1966.

Work on the surface ionization detector for hydrogen will be de-
voted to a mass spectrometric investigation of the ion species emitted.
There are some signs of renewed interest in a detector for CO and we hope
to repeat some of the CO/air tests reported earlier.

Discussions with the Jet Propulsion Laboratory regarding a con-
tract for development of a Field Ionization Source are still continuing.
We hope to begin work on this contract within the next six months.

This contract will bring us closer to an operating NASA facility
and seems to offer an avenue for use of our results in exploration of the
moon and the planets.

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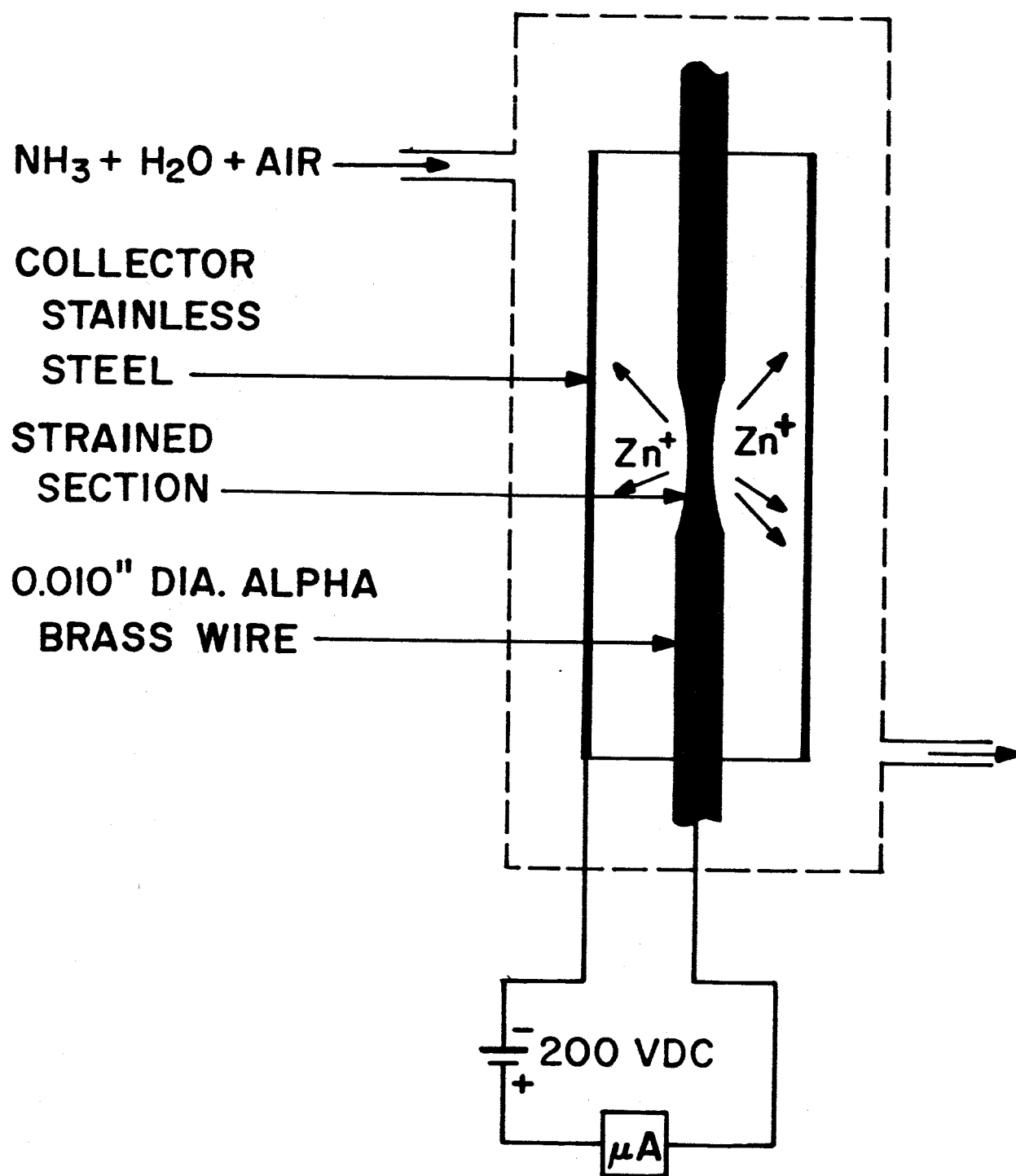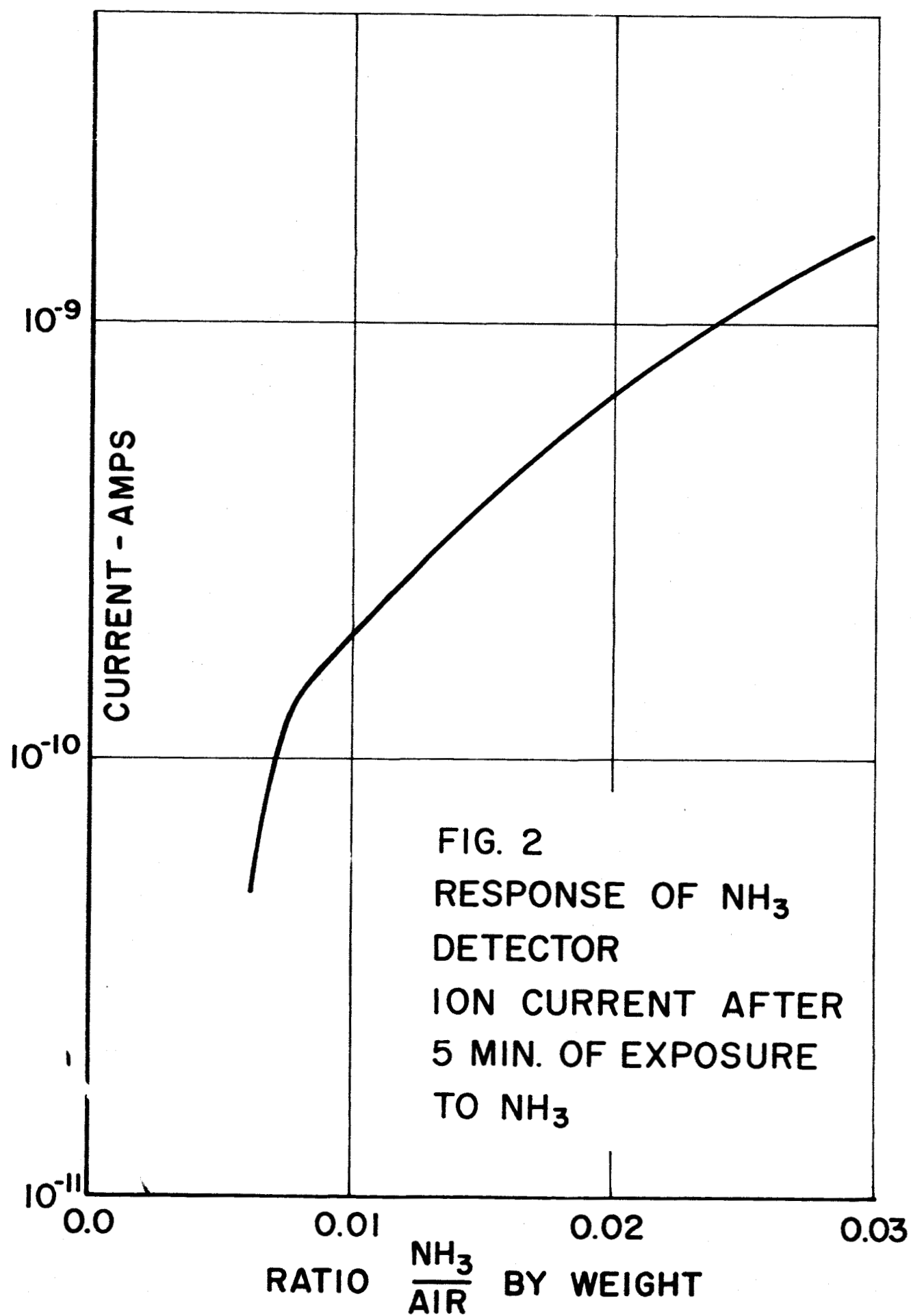7. A Low Cost, High Temperature ($1300^{\circ}C$) Vacuum Furnace. Accepted by J. Vacuum Science and Technology.

NH₃ + H₂O + AIR ——→

COLLECTOR
  STAINLESS
    STEEL ——————→

STRAINED
  SECTION ——————→

0.010" DIA. ALPHA
  BRASS WIRE ——————→

Zn^+ Zn^+

200 VDC

μA

FIG. I
AMMONIA VAPOR
DETECTOR SYSTEM

FIG. 2
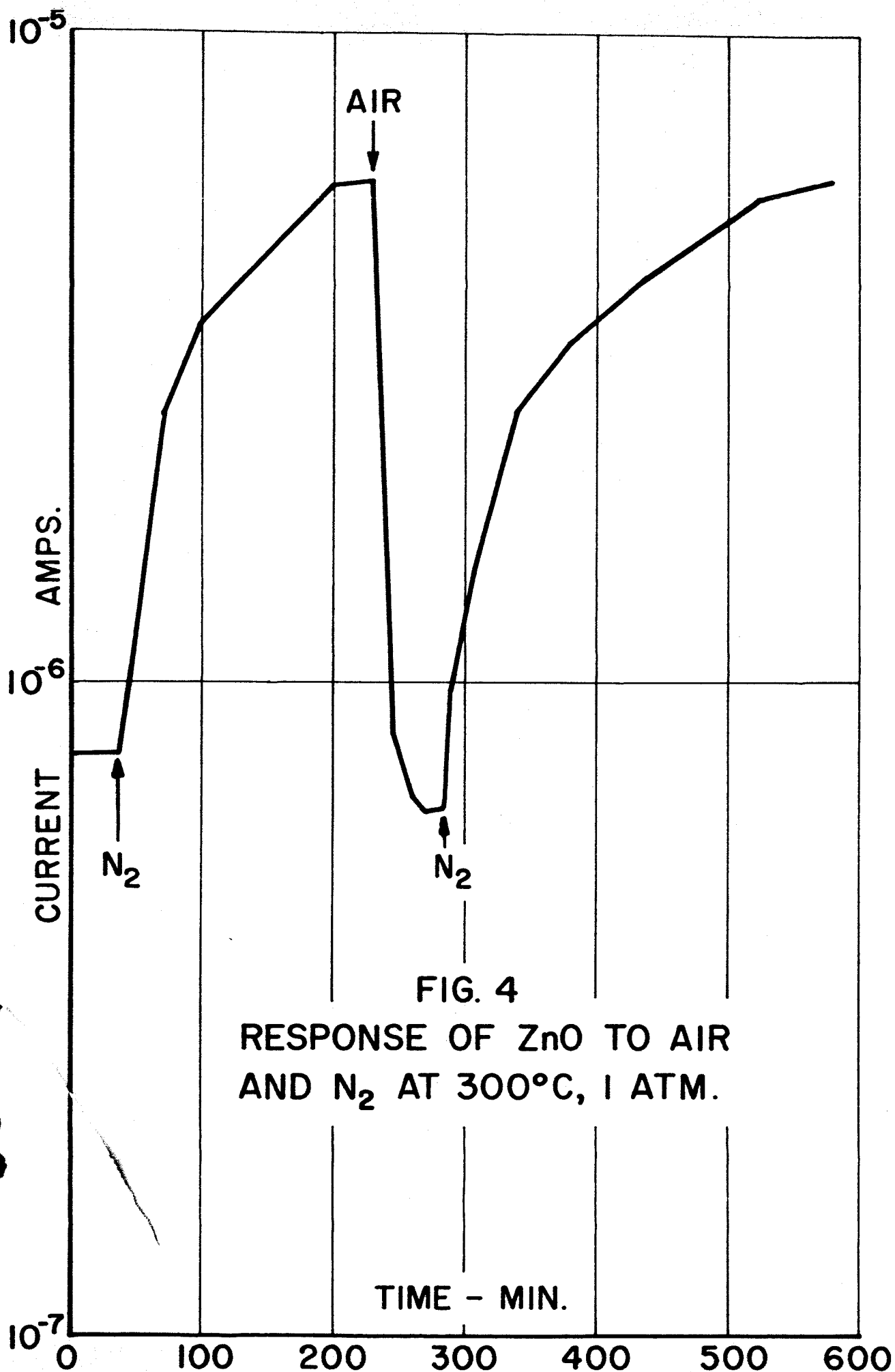RESPONSE OF NH_3
DETECTOR
ION CURRENT AFTER
5 MIN. OF EXPOSURE
TO NH_3

FIG. 4
RESPONSE OF ZnO TO AIR
AND N₂ AT 300°C, I ATM.

PRESSURE TORR

FIG. 5

TYPICAL RESPONSE
OF ZnO TO AIR AND
N_2 AT 300°C

N_2

AIR